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Supporting Information

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Highly Enantio- and Regioselective Quinone Diels-Alder Reactions Catalyzed by a Tridentate Cr(III) Complex

Elizabeth R. Jarvo, Brian M. Lawrence, Eric N. Jacobsen

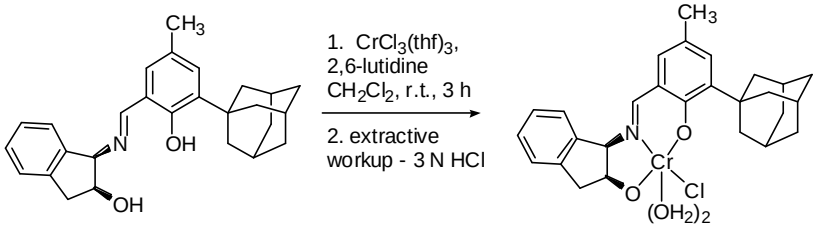
Department of Chemistry and Chemical Biology
Harvard University, Cambridge MA 02138

Part 1. Experimental Procedures and Analytical Data
a. General Procedures

Analytical thin-layer chromatography (TLC) was performed on silical gel 60 F_{254} precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV light and/or staining with anisaldehyde, ceric ammonium molybdate (CAM), or vanillin solutions. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. Proton and carbon NMR spectra were recorded on a Varian Mercury-400 (400 MHz), Inova-500 (500 MHz), or an Inova-600 (600 MHz) spectrometer. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the respective solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm; C_6D_6, δ 7.16 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m), broad (br)], coupling constants [Hz], integration). Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0). NMR data were collected at ambient temperature. Infrared spectra were obtained as thin films between NaCl plates on a Matteson FTIR 3000. Optical Rotations were measured using a 2 mL cell with a 1 dm length on a Jasco DIP 370 polarimeter. Circular dichroism spectra were aquired on a Jasco J-710 Spectropolarimeter. Mass spectra were obtained at the Mass Spectrometry Facilities of Harvard University (Cambridge, MA). The method of ionization is given in parentheses. Analytical HPLC was performed on a Shimadzu VP-series instrument employing a dual-wavelength UV detector (214, 254 nm) and the column specified in the individual experiment.

All reactions were carried out under inert atmosphere employing oven- and flame-dried glassware. Unless otherwise stated, all reagents were purchased from Aldrich, Alfa Aesar or Strem and used without further purification. All solvents were distilled from appropriate drying agents prior to use. 5 Å molecular sieves (3.2 mm pellet, Aldrich) were crushed and dried in a vacuum oven (135 °C) prior to use. Ligand **7** and catalyst **8** were prepared as previously reported.[*] Quinone **3**[†] and 2,3-dimethyl quinone[‡] were prepared by the literature procedures and were purified by flash chromatography before use. (Note: quinone **3** is quite volatile and prone to sublimation, even at 0 °C, and so should be chromatographed with 5% EtO_2/pentanes and be stored at -30 °C.) *p*-Benzoquinone and naphthoquinone were purified by sublimation prior to use. Unless otherwise stated, dienes were prepared by the literature procedure from the corresponding commercially available enones by reaction with TESOTf and NEt_3 in ether at -78 °C to r.t.[§] Diene **11** was prepared from (*E*)-6-methyl-2-hepten-4-one[**] by reaction with TESCl and KHMDS in ether at -78 °C to r.t.[††] 1-Hydroxy-7-nonen-6-one was prepared by the literature procedure[‡‡] and reacted with TESOTF and NEt_3 in ether at -78 °C to afford the desired diene. All dienes were purified by distillation under reduced pressure or by silica gel chromatography prior to use. DBU was distilled over CaO before use.

b. Catalyst Preparation



7 **9**

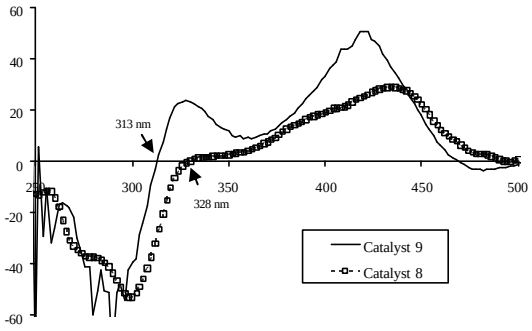
In the glovebox, a flask was charged with $CrCl_3$•3THF (2.33 g, 6.23 mmol, 1.00 equiv.) and was sealed with a septum. The flask was removed from the glovebox, placed under an atmosphere of N_2, and (*1R,2S*)-ligand **5** (2.50 g, 6.23

[*] K. Gademann, D. E. Chavez, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2002**, *41*, 3059-3061.
[†] a) I.M. Godfrey, M.V. Sargent, J.A. Elix, *J.Chem. Soc. Perkins 1* **1974**, 1353-1354. b) J.R. Luly, H.Rapoport, *J. Org. Chem.* **1981**, *46*, 2745-2752.
[‡] H. Buff, U. Kucklander, *Tetrahedron* **2000**, *56*, 5137-5145.
[§] D.A. Oare, M.A. Henderson, M.A. Sanner, C.H. Heathcock, *J. Org. Chem.* **1990**, *55*, 132-157.
[**] R.A. Pilli, L.C. Diaz, A.O. Malaner, *J. Org. Chem.* **1995**, *60*, 717-722.
[††] M. Arisawa, Y. Torisawa, M. Nakagawa, *Synthesis*, **1995**, 1371-1372.
[‡‡] M. Ihara, S. Suzuki, N. Taniguchi, K. Fukumoto, C. Kabuto, *J. Chem. Soc. Perkins Trans 1* **1992**, 2527-2535.

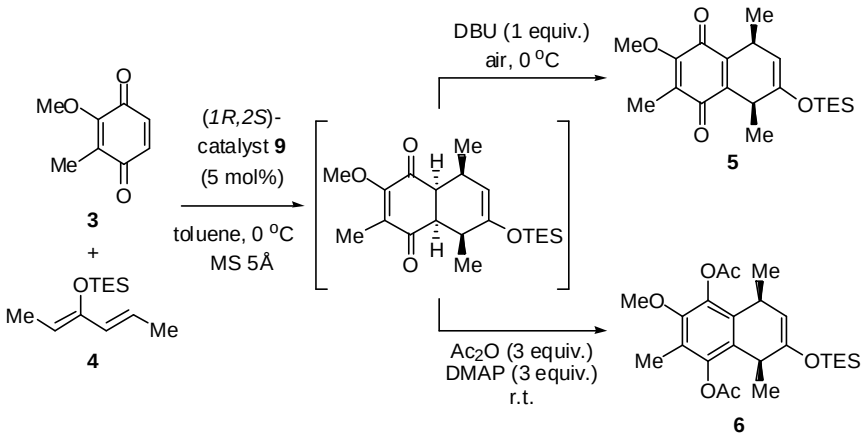
mmol, 1.00 equiv.) and CH_2Cl_2 (48 mL) were added. The reaction mixture was stirred and 2,6-lutidine (1.45 mL, 12.5 mmol, 2.00 equiv.) was added dropwise. After stirring at room temperature 16 h, the reaction mixture was diluted with CH_2Cl_2 (875 mL), transferred to a separatory funnel, and washed *very gently* with three portions of 3 N HCl (200 mL). Excessive shaking of the extraction results in the formation of emulsions and reduces the yield and purity of the product. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Acetone (200 mL) was added to the dark brown solid and the flask was sealed and allowed to stand at 4 °C for 18 h, after which time a small quantity of green solid had formed. The mixture was filtered through filter paper (without washing, all solid material was discarded) and the filtrate was concentrated and dried *in vacuo* to afford (*1R,2S*)-catalyst **9** (2.60 g, 4.97 mmol, 79.8% yield) as a dark brown powder. **IR** (KBr pellet) 3075, 2903, 2847, 2656, 1680, 1612, 1537, 1477, 1431, 1338, 1303, 1229, 1171, 1097, 1074, 980, 837, 746; **MS** (CI^+) calc. for $C_{28}H_{36}ClCrNO_6$ (M+H+formic acid) 569, found 569.

Crystals suitable for X-ray analysis were grown by slow evaporation of a solution of pentane:benzene:acetone (1:1:0.2) at 4°C for 1 month. See Part 3a for details.

CD spectra for catalysts **8** and **9** (in CH_2Cl_2) are shown below.[§§]



b. Quinone Diels-Alder Reactions
i. Standard Procedure



A 25 mL round-bottomed flask charged with 5 Å molecular sieves (250 mg) was flame-dried *in vacuo*. (*1R,2S*)-Catalyst **9** (26.0 mg, 0.0500 mmol, 5 mol%), quinone **3** (152.1 mg, 1.000 mmol, 1.000 equiv) and toluene (5 mL) were added and the mixture was stirred at room temperature for 5 min, then cooled to 0 °C (for 15 min). Diene **4** (354 µL, 1.10 mmol, 1.10 equiv.) was added dropwise (1 drop/20 seconds) via syringe. Reaction progress was monitored by TLC; after 45 min all quinone **3** had been consumed (Note: any remaining quinone starting material will lower yields in subsequent oxidation reactions, and so reactions must be monitored attentively). *In situ* derivatization of the

[§§] Comparison of the CD spectra of Cr(Schiff base) complexes can aid in structure determination. R.T.Ruck, E.N. Jacobsen, unpublished results.

intermediate cycloadduct (R_f = 0.60, 20% EtOAc/hexanes) was performed according to one of the following procedures to facilitate isolation.

Oxidation to Quinone 5

The reaction was immediately diluted with toluene (2.5 mL) and cooled to 0 ^oC. The septum was removed, the reaction was stirred under ambient atmosphere, and DBU (150 µL, 1.00 mmol, 1.00 equiv.) was added dropwise via syringe. The reaction changed color from brown to green and then red over the course of 40 minutes, at which point no intermediate cycloadduct remained (as judged by TLC). The reaction was *immediately* applied directly to silica gel chromatography, rinsing the flask with hexanes. Excess diene was eluted with hexanes and the desired product was eluted with a gradient of 0.5-1-2% EtOAc/hexanes. Quinone **5** was isolated as a bright yellow oil (293.7 mg, 0.810 mmol, 81.0% yield). The product was determined to be 96% ee, 12:1 regioisomer ratio by chiral HPLC analysis [(*S*,*S*)-Whelk-O (Regis) in tandem with YMC-Pack Diol-NP (YMC, Inc.), prewash 5% EtOH/hexanes, 0.6 mL/min, for 5 min, preequilibrate 0.05% EtOH/hexanes, 0.6 mL/min, for 20 min, run 0.05% EtOH/hexanes, 0.6 mL/min. Major regioisomer: t_r= 16.5 min (major enantiomer), 20.1 min (minor enantiomer). Minor regioisomer: t_r = 18.8 min (both enantiomers). See section 1d for a sample HPLC trace].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.85 (d, J = 4.8 Hz, 1H), 3.98 (s, 3H), 3.45 (m, 1H), 3.24 (dq, J = 7.0, 3.0 Hz, 1H), 1.94 (s, 3H), 1.29 (d, J = 6.9 Hz, 3H), 1.18 (d, J = 7.0 Hz, 3 H), 0.97 (t, J = 7.9 Hz, 9H), 0.69 (q, J = 7.9 Hz, 6); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 187.4, 182.2, 155.5, 152.0, 143.4, 142.1, 128.7, 104.4, 60.8, 34.2, 30.2, 23.5, 21.1, 8.7, 6.7, 5.0; **IR** (thin film) 2969, 2883, 1683, 1658, 1618; **TLC R_f** 0.76 (20% EtOAc/hexanes); **[a]$_D^{25}$** -37.6 (*c*= 1.0; toluene); **MS** (CI^+) calc. for $C_{20}H_{32}O_4Si$ (M+2H, hydroquinone) 364, found 364.

Protection as Hydroquinone 6

Acetic anhydride (472 µL, 5.00 mmol, 5.00 equiv.), N,N-dimethylaminopyridine (DMAP, 122 mg, 1.00 mmol, 1.00 equiv.), and NEt_3 (1.40 mL, 10.0 mmol, 10.0 equiv.) were added to the reaction mixture. The reaction was allowed to warm to room temperature and stirred for 16 hours, and which point no intermediate cycloadduct was present as judged by TLC. A small quantity of a side product arising from deprotection of the silyl enol ether to afford the ketone was observed (R_f = 0.20, 20% EtOAc/hexanes). The reaction mixture was applied directly to silica gel chromatography (gradient elution: 0-60% EtOAc/hexanes) to afford product **6** as a colorless glassy oil (363.0 mg, 0.809 mmol, 80.9% yield).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.95 (d, J = 5.5 Hz, 1H), 3.73 (s, 3H), 3.44 (br s, 1H), 3.09 (very br s, 1H), 2.34 (s, 6H), 2.06 (s, 3H), 1.32 (br s, 3H), 1.21 (d, J = 6.6 Hz, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.69 (q, J = 7.8 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 168.7, 168.6, 152.8, 148.5, 144.7, 139.4, 131.4, 129.1, 123.2, 105.1, 60.7, 35.0, 30.7, 24.0, 21.5, 20.6, 20.5, 9.4, 6.6, 4.9; **IR** (thin film) 2959, 2932, 2878, 1762, 1679; **TLC R_f** 0.45 (20% EtOAc/hexanes); **[a]$_D^{25}$** -22.8 (*c*= 0.795; CH_2Cl_2); **MS** (CI^+) calc. for $C_{24}H_{37}O_6Si$ (M+H) 449.2359, found 449.2358.

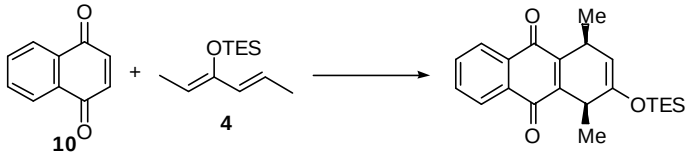
Notes:

1) Oxidations that prove to be more prone to decomposition may in some cases be improved by catalysis by Co(salen) or salcomine.[***]
2) Acylation reactions should be monitored as prolonged exposure to acylation conditions may lead in some cases to deprotection of the silyl enol ether to afford the ketone.

ii. Data for Substrates (Table 2, entries 2-4; Table 3, entries 1-9).

Table 2, Entry 2

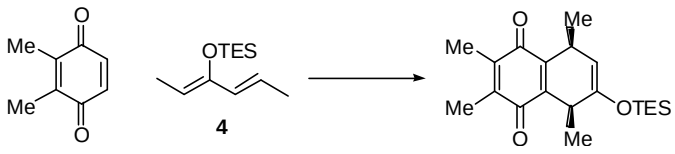
[***] a) G.A. Kraus, P.K. Choudhury, *J. Org. Chem.* **2002**, *67*, 5857-5859. b) B.H. Lipshutz, P. Mollard, S.S. Pfeiffer, W. Chrisman, *J. Am. Chem. Soc.* **2002**, *124*, 14282-14283.



The standard procedure for the quinone DA reaction was utilized with the following modification: reaction time = 10 min. The intermediate cycloadduct (R_f = 0.70, 20% EtOAc/hexanes) was oxidized according to the standard procedure. The product, a yellow solid, was found to be 94% ee by chiral HPLC analysis [(*S*,*S*)-Whelk-O (Regis), prewash 5% EtOH/hexanes, 0.6 mL/min, for 5 min, preequilibrate 0.1% EtOH/hexanes, 0.6 mL/min, for 20 min, run 0.1% EtOH/hexanes, 0.6 mL/min. t_r= 20.9 min (major enantiomer), 24.6 min (minor enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (m, 2H), 7.69 (m, 2H), 4.92 (d, J=5.1 Hz, 1H), 3.66 (m, 1H), 3.44 (dq, J = 6.9, 2.6 Hz, 1H), 1.38 (d, J = 6.9 Hz, 3 H), 1.26 (d, J = 6.9 Hz, 3H), 0.99 (t, J = 7.8 Hz, 9H), 0.71 (q, J = 7.9 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 184.1 (2C), 152.0, 146.5, 146.1, 133.4, 133.4, 132.3, 132.2, 126.3, 126.2, 104.3, 34.4, 30.8, 23.6, 20.9, 6.7, 5.0; **IR** (thin film) 3307, 3073, 2959, 2878, 1663, 1622, 1601; **TLC R_f** 0.81 (20% EtOAc/hexanes); **[**a**]$_D^{25}$** +7.9 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{22}H_{29}O_3Si$ (M+H) 369, found 369; **m.p.** 40-42 °C.

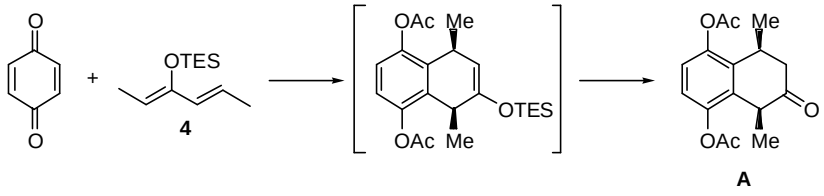
Table 2, Entry 3

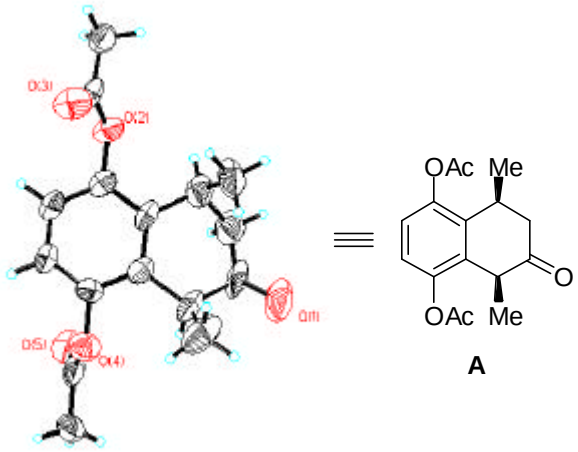


The standard procedure for the quinone DA reaction was utilized with the following modification: reaction time = 30 min. The intermediate cycloadduct (R_f = 0.63, 20% EtOAc/hexanes) was oxidized according to the standard procedure. The product, a yellow oil, was found to be 94% ee by chiral HPLC analysis [(*S*,*S*)-Whelk-O (Regis), prewash 5% EtOH/hexanes, 0.6 mL/min, for 5 min, preequilibrate 0.1% EtOH/hexanes, 0.6 mL/min, for 20 min, run 0.1% EtOH/hexanes, 0.6 mL/min. t_r= 14.9 min (major enantiomer), 17.3 min (minor enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.86 (d, J = 4.8 Hz, 1H), 3.46 (m, 1H), 3.24 (dq, J = 6.9, 3.0 Hz, 1H), 2.01 (s, 6H), 1.28 (d, J = 7.0 Hz, 3H), 1.18 (d, J = 7.0 Hz, 3H), 0.98 (t, J = 7.9 Hz, 9H), 0.69 (q, J = 7.8 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 186.6, 186.5, 152.0, 143.5, 143.2, 140.5 (2C), 104.6, 34.0, 30.4, 23.6, 20.9, 12.2, 6.7, 5.0 (2C); **IR** (thin film) 3282, 2959, 2874, 1682, 1653; **TLC R_f** 0.72 (20% EtOAc/hexanes); **[**a**]$_D^{25}$** +5.1 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{20}H_{33}O_3Si$ (M+H) 349, found 349.

Table 2, Entry 4



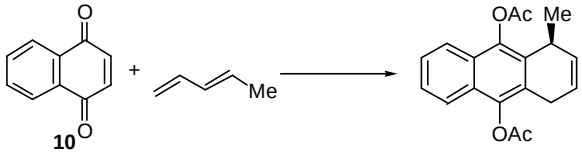


A

The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, reaction temp = -40 °C, reaction time = 3 h. The intermediate cycloadduct (R_f = 0.61, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone (R_f = 0.54, 20% EtOAc/hexanes), which was directly treated with a 0.5% solution of TFA in CH_2Cl_2 at room temperature for 10 minutes to afford the desired ketone **A** as a white solid (isolated yield reflects three step procedure). The product was found to be 86% ee by chiral HPLC analysis [Chiracel OD (Daicel), 2% EtOH/hexanes, 1 mL/min. t_r = 20.6 min (minor enantiomer), 28.5 min (major enantiomer)]. The relative stereochemistry of the product was confirmed by x-ray crystal structure analysis of single crystals grown by slow evaporation of a solution in CH_2Cl_2 over pentane (see Part 3 for full details).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.00 (s, 2H), 3.46 (q, J = 7.4 Hz, 1H), 3.41 (m, 1H), 2.70 (dd, J = 15.1, 5.4 Hz, 1H), 2.54 (d, J = 15.1 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.44 (d, J = 7.3 Hz, 3H), 1.16 (d, J = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 211.5, 169.3, 169.0, 146.3, 145.1, 134.3, 132.7, 121.6, 121.4, 45.8, 41.5, 28.8, 21.8, 20.9, 20.8, 18.4; **IR** (thin film) 2980, 2940, 1763, 1717; **TLC R_f** 0.083 (20% EtOAc/hexanes); **$[\alpha]_D^{25}$** -148.6 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{16}H_{22}O_5N$ ($M+NH_4$) 308, found 308; **m.p.** 95-96 °C.

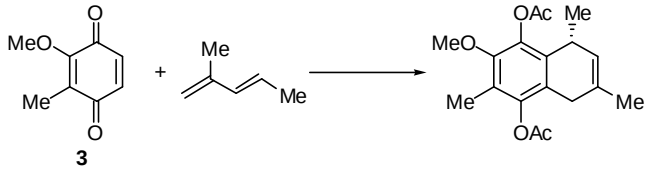
Table 3, Entry 1



The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv. diene = 3, reaction time = 14 h. (The reaction was monitored by ^{1}H NMR as the Rf of the starting quinone and cycloadduct are the same.) The intermediate cycloadduct (R_f = 0.38, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product, a white solid, was found to be 90% ee by chiral HPLC analysis [Chiralpak AD (Daicel), 1% *i*-PrOH/hexanes, 1 mL/min. t_r = 10.3 min (minor enantiomer), 12.9 min (major enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (br m, 2H), 7.50 (m, 2H), 6.00 (br m, 1H), 5.92 (br dt, J = 9.9, 3.5 Hz, 1H), 3.61 (br s, 1H), 3.45 (br m, 1H), 3.28 (br m, 1H), 2.52 (s, 3H), 2.50 (s, 3H), 1.33 (br d, J = 6.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.3, 168.8, 141.5, 130.6, 130.4, 126.9, 126.3, 126.2, 126.0, 125.0, 122.0, 121.3, 121.1, 117.6, 30.2, 24.3, 21.9, 20.7, 20.5; **IR** (thin film) 3422, 3072, 3034, 2967, 2930, 2872, 1762; **TLC R_f** 0.35 (20% EtOAc/hexanes); **$[\alpha]_D^{25}$** +93.1 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{19}H_{22}O_4N$ ($M+NH_4$) 328, found 328; **m.p.** 113-125 (decomp).

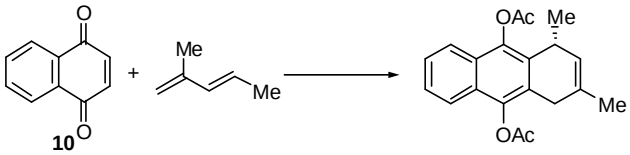
Table 3, Entry 2



The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv. diene = 1.5, reaction temp = -40 °C, reaction time = 15 h, and (*1S,2R*)-catalyst **9** was employed. The intermediate cycloadduct (R_f = 0.50, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product, a clear, colorless oil, was found to be 93% ee and with >30:1 regioselectivity by chiral HPLC analysis [Chiracel OD-H (Daicel), 4% *i*-PrOH/hexanes, 1 mL/min. t_r= 6.1 min (major enantiomer), 7.2 min (minor enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.53 (m, 1H), 3.73 (s, 3H), 3.35 (br s, 1H), 2.97 (br s, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 2.08 (s, 3H), 1.77 (s, 3H), 1.16 (d, J = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 168.9, 168.7, 148.6, 144.9, 139.7, 131.5, 129.2, 124.8, 123.6, 122.5, 60.8, 30.7, 28.9, 23.0, 22.4, 20.6, 20.5, 9.8; **IR** (thin film) 3519, 2976, 2934, 2874, 1760; **TLC R_f** 0.081 (20% EtOAc/hexanes); **[**a**]$_D^{25}$** -51.3 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{18}H_{26}O_5N$ ($M+NH_4$) 336, found 336.

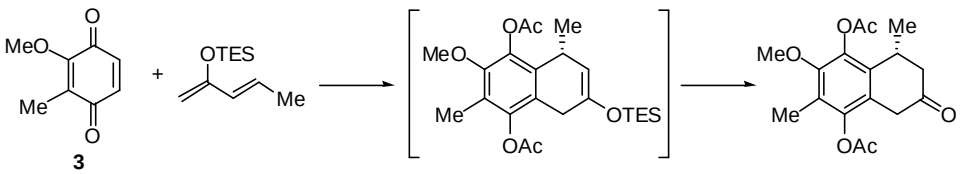
Table 3, Entry 3



The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv. diene = 1.5, reaction time = 1.5 h, and (*1S,2R*)-catalyst **9** was employed. The intermediate cycloadduct (R_f = 0.48, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product was found to be 91% ee by chiral HPLC analysis [Chiracel OD (Daicel), 1% *i*-PrOH/hexanes, 1 mL/min. t_r= 20.1 min (minor enantiomer), 26.1 min (major enantiomer)].

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (m, 2H), 7.22 (m, 2H) 5.42 (br s, 1H), 3.61 (br s, 1H), 3.23 (d, J = 21.0 Hz, 1H), 3.17 (d, J = 21.0 Hz, 1H), 1.89 (s, 3H), 1.88 (s, 3H), 1.59 (br s, 3H), 1.24 (br d, J = 7.3 Hz, 3H); **^{13}C NMR** (C_6D_6, 125 MHz) δ 168.4, 168.0, 142.2, 142.1, 130.8, 129.5, 127.1, 126.8, 126.4, 126.3, 125.9, 125.4, 121.9, 121.6, 31.6, 29.5, 23.1, 22.3, 20.1, 19.9; **IR** (thin film) 3069, 2969, 2930, 2870, 1761; **TLC R_f** 0.33 (20% EtOAc/hexanes); **[**a**]$_D^{25}$** -90.4 (*c*= 1.00; CH_2Cl_2); **MS** (ES^+) calc. for $C_{20}H_{24}O_4N$ ($M+NH_4$) 342, found 342.

Table 3, Entry 4

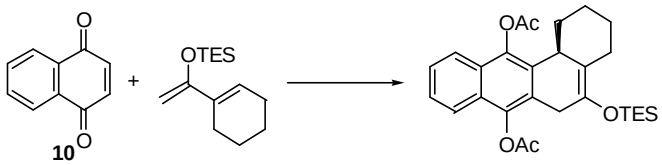


The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, reaction temp = -40 °C, equiv. diene = 1.5, reaction time = 1 h, and (*1S,2R*)-catalyst **9** was employed. The intermediate cycloadduct (R_f = 0.54, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone (R_f = 0.41, 20% EtOAc/hexanes), which was directly treated with a 5% solution of TFA in CH_2Cl_2 at room temperature for 10 minutes to afford the desired ketone as a clear, colorless oil (isolated yield

reflects three step procedure). The product was found to be 97% ee and with 25:1 regioselectivity by chiral HPLC analysis [Chiracel OD-H (Daicel), 2% EtOH/hexanes, 1 mL/min. Major regioisomer: t_r= 14.7 min (minor enantiomer), 19.9 min (major enantiomer). Minor regioisomer: t_r= 15.7 min, 18.6 min].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71 (s, 3H), 3.38 (br m, 2H), 3.23 (br m, 1H), 2.64 (dd, J = 15.2, 5.7 Hz, 1H), 2.45 (dd, J = 15.2, 2.0 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 2.04 (s, 3H), 1.08 (d, J = 7.33 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ ;208.2, 168.8, 168.2, 149.2, 145.2, 139.0, 132.1, 124.0, 121.5, 60.7, 45.5, 37.2, 29.3, 20.5, 20.3, 20.1, 9.7; **IR** (thin film) 2963, 2936, 1763, 1729; **TLC R_f** 0.12 (20% EtOAc/hexanes); **[a]$_D^{25}$** +103.6 (*c*= 1.0; CH_2Cl_2); **MS** (ES^+) calc. for $C_{17}H_{24}O_6N$ ($M+NH_4$) 338, found 338;

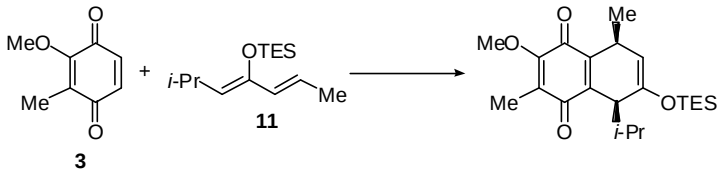
Table 3, Entry 5



The standard procedure for the quinone DA reaction was utilized with the following modifications: equiv. diene = 1.5, reaction time = 25 min. The intermediate cycloadduct (R_f = 0.64, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product, a light yellow oil, was found to be 90% ee by chiral HPLC analysis [Chiracel OD (Daicel), 0.5% *i*-PrOH/hexanes, 1 mL/min. t_r= 16.7 min (major enantiomer), 22.2 min (minor enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, 2H), 7.45 (m, 2H), 3.40 (br m, 3H), 3.04 (br dt, J = 13.0, 1.6 Hz, 1H), 2.50 (s, 3H), 2.48 (overlapping s and m, 4H), 1.92 (br d, J = 12.8 Hz, 1H), 1.84 (br d, J = 12.4 Hz, 1H), 1.60 (br overlapping m, 2H), 1.39 (br m, 1H), 1.31 (br m, 1H), 1.04 (t, J = 7.9 Hz, 9 H), 0.73 (q, J = 7.9 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.2, 168.7, 141.4, 141.3, 136.4, 128.5, 126.4, 126.3 (2C), 126.0, 124.8, 121.3, 121.0, 116.3, 40.8, 36.0, 29.3, 27.5, 26.9, 20.8, 20.4, 6.8, 5.8, 5.5; **IR** (thin film) 3374, 2938, 1760; **TLC R_f** 0.55 (20% EtOAc/hexanes); **[a]$_D^{25}$** +73.6 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{28}H_{40}O_5SiN$ ($M+NH_4$) 498, found 498.

Table 3, Entry 6

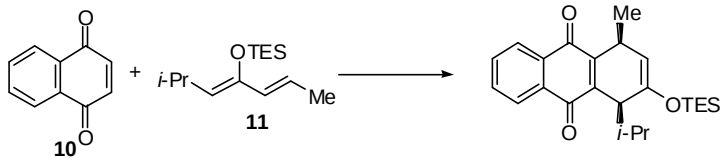


The standard procedure for the quinone DA reaction was utilized with the following modifications: catalyst loading = 10 mol%, equiv. diene = 1.2, [quinone] = 0.8 M, reaction time = 20 h. The intermediate cycloadduct (R_f = 0.46, 20% EtOAc/hexanes) was oxidized according to the following modified procedure. Upon complete consumption of **1**, the reaction mixture was diluted to 0.1 M with toluene ([cycloadduct]), the septum was removed, and the reaction was cooled to 0 ^{o}C. A solution of DBU (1 equiv., 0.2 M in toluene) was added over 30 minutes using a syringe pump, after which time the reaction mixture was *immediately* applied to silica gel chromatography (0-1-2% EtOAc/hexanes). This afforded the desired product as a yellow oil (75% yield). The product was found to be 90% ee and with 9:1 regioselectivity by chiral HPLC analysis [(*S,S*)-Whelk-O (Regis) in tandem with YMC-Pack Diol-NP (YMC, Inc.), prewash 5% EtOH/hexanes, 0.6 mL/min, for 5 min, preequilibrate 0.05% EtOH/hexanes, 0.6 mL/min, for 20 min, run 0.05% EtOH/hexanes, 0.6 mL/min. Major regioisomer: t_r= 15.4 min (major enantiomer), 19.0 min (minor enantiomer). Minor regioisomer: t_r = 17.9 min (both enantiomers)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.88 (d, J = 4.9 Hz, 1H), 3.99 (s, 3H), 3.47 (m, 1H), 3.20 (t, J = 3.4 Hz, 1H), 1.94 (s, 3H), 1.90 (m, 1H), 1.25 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 7.3 Hz, 3H), 0.98 (t, J = 7.8 Hz, 9H); 0.87 (d, J = 6.8 Hz, 3H), 0.69 (q, J = 8.0 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 187.8, 182.7, 155.4, 149.5, 143.0, 142.5, 128.5, 105.9, 60.8,

44.5, 32.4, 30.6, 22.9, 22.3, 19.1, 8.8, 6.8, 5.0; **IR** (thin film) 2965, 2884, 1657, 1617; **TLC R_f** 0.80 (20% EtOAc/hexanes); **[a]$_D^{25}$** -59.3 (*c*= 0.740; CH_2Cl_2); **HRMS** (ES^+) calc. for $C_{22}H_{35}O_4Si$ (M+H) 391.2305, found 391.2305.

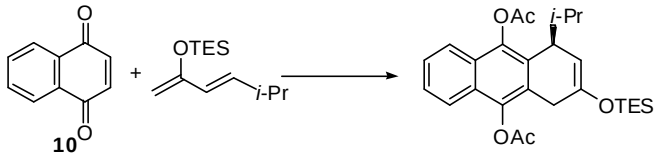
Table 3, Entry 7



The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv. diene = 1.2, reaction temp = -20 °C, reaction time = 43 h. The intermediate cycloadduct (R_f = 0.57, 20% EtOAc/hexanes) was oxidized according to the modified procedure reported above for Table 3, Entry 6. The product, a yellow solid, was found to be 87% ee by chiral HPLC analysis [(*R*,*R*)-Whelk-O (Regis) in tandem with YMC-Pack Diol-NP (YMC, Inc.), prewash 5% EtOH/hexanes, 0.6 mL/min, for 5 min, preequilibrate 0.05% EtOH/hexanes, 0.6 mL/min, for 20 min, run 0.05% EtOH/hexanes, 0.6 mL/min. t_r= 23.7 min (minor enantiomer), 27.2 min (major enantiomer)].

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (m, 2H), 7.70 (m, 2H), 4.96 (d, J = 5.4 Hz, 1H), 3.68 (m, 1H), 3.53 (t, J = 3.7 Hz, 1H), 2.00 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H), 1.15 (d, J = 6.8 Hz, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.92 (d, J = 6.8 Hz, 3H), 0.71 (q, J = 8.0 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 184.7, 184.1, 149.6, 146.9, 145.9, 133.4, 133.3, 132.5, 132.3, 126.3, 126.2, 105.8, 44.8, 32.8, 31.3, 23.0, 22.5, 19.4, 6.8, 5.0; **IR** (thin film) 2968, 2883, 1665, 1622; **TLC R_f** 0.76 (20% EtOAc/hexanes); **[a]$_D^{25}$** +10.5 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{24}H_{36}O_3SiN$ ($M+NH_4$) 414, found 414; **m.p.** 39-45 °C.

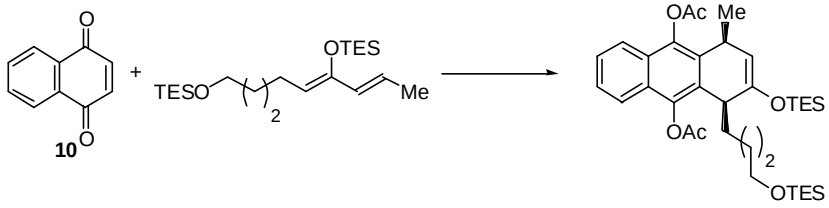
Table 3, Entry 8



The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv diene = 3, reaction temp = -40 °C, reaction time = 19 h. The intermediate cycloadduct (R_f = 0.64, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product, a clear oil, was found to be 96% ee by chiral HPLC analysis [Chiracel OD (Daicel), 0.25% *i*-PrOH/hexanes, 1 mL/min. t_r= 22.9 min (major enantiomer), 27.8 min (minor enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (br m, 1H), 7.67 (br m, 1H), 7.50 (m, 2H), 5.04 (d, J = 5.5 Hz, 1H), 3.59 (br s, 1H), 3.31 (br m, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 2.25 (br s, 1H), 1.02 (overlapping d and t, J = 5.9 Hz, 7.8 Hz, respectively, 12 H), 0.76 (q, J = 7.7 Hz, 6H), 0.62 (br d, J = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.2, 168.7, 149.2 (2C), 141.2, 129.3, 126.5, 126.4 (2C), 126.3, 126.1, 121.4, 121.1, 99.6, 42.4, 39.9, 30.0, 21.3, 20.8, 20.6, 16.6, 6.7, 4.9; **IR** (thin film) 3417, 2968, 2883, 1765, 1682; **TLC R_f** 0.52 (20% EtOAc/hexanes); **[a]$_D^{25}$** +62.7 (*c*= 1.0; CH_2Cl_2); **MS** (CI^+) calc. for $C_{27}H_{40}O_5SiN$ ($M+NH_4$) 486, found 486.

Table 3, Entry 9

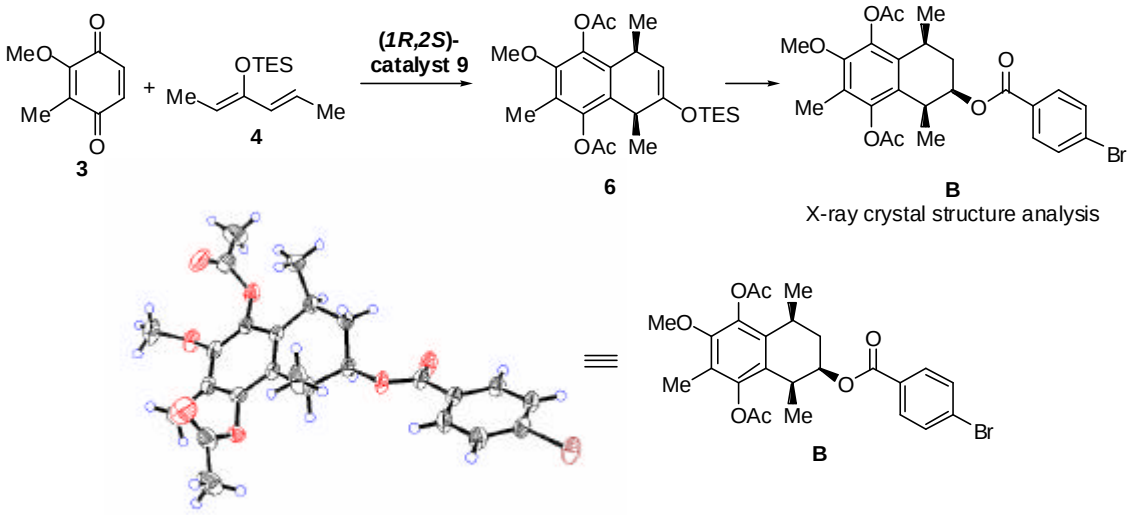


The standard procedure for the quinone DA reaction was utilized with the following modifications: [quinone] = 0.8 M, equiv. diene = 3, reaction time = 1 h. The intermediate cycloadduct (R_f = 0.68, 20% EtOAc/hexanes) was derivatized according to the standard procedure to give the corresponding hydroquinone. The product, a clear oil, was found to be 91% ee by chiral HPLC analysis [(S,S)-Whelk-O (Regis), 1.5% EtOH/hexanes, 1 mL/min. t_r= 18.5 min (minor enantiomer), 21.3 min (major enantiomer)].

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (br s, 2H), 7.46 (m, 2H), 5.06 (d, J = 5.5 Hz, 1H), 3.56 (overlapping m and br t, J = 6.0 Hz, 3H), 3.40 (very br m, 1H), 2.49 (s, 6H), 1.84 (br m, 2H), 1.58 (br m, 2H), 1.36 (br m, 2H), 0.98 (t, J = 7.9 Hz, 9H), 0.92 (t, J = 8.0 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H), 0.56 (q, J = 7.9 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.0 (2C), 151.8, 141.6, 141.3, 130.5, 126.2, 126.1 (2C), 121.4, 121.3, 105.8, 62.7, 40.4 (2C), 36.3 (2C), 33.2, 31.2 (2C), 23.9, 23.3, 20.7, 6.7 (2C), 4.9, 4.3; **IR** (thin film) 3436, 1776, 1644; **TLC R_f** 0.55 (20% EtOAc/hexanes); **[α]$_D^{25}$** -27.0 (*c*= 0.74; CH_2Cl_2); **MS** (CI^+) calc. for $C_{35}H_{58}O_6Si_2N$ ($M+NH_4$) 644, found 644.

Part 2. Proof of Absolute Stereochemistry

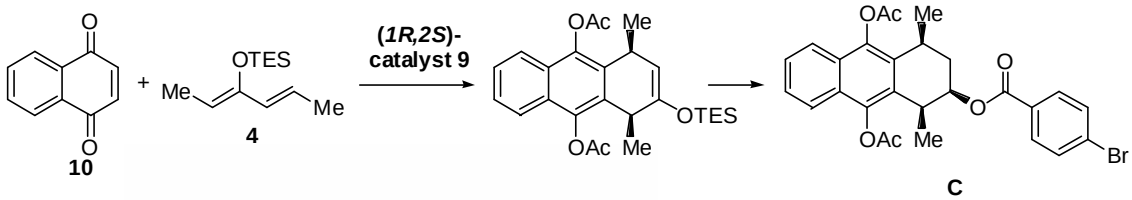
a. Table 2, Entry 1 (*p*-Bromobenzoate **B**)



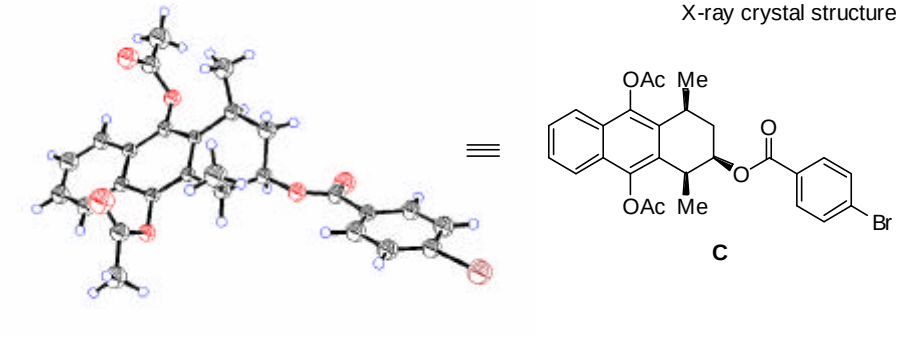
The quinone DA reaction (1 mmol scale) and derivatization was performed under the standard conditions using (*1R,2S*)-catalyst **9**. The silyl enol ether (320.0 mg, 0.71 mmol) was dissolved in CH_2Cl_2 (15 mL) and TFA (1 mL) was added. The reaction was stirred at r.t. for 10 min, at which time the starting material had been consumed (as observed by TLC). The reaction mixture washed twice with saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo*. The unpurified ketone (237 mg, 0.71 mmol, 1.00 equiv.) was dissolved in methanol (12 mL), cooled to 0 °C, $NaBH_4$ (67.0 mg, 1.78 mmol, 2.5 equiv.) was added, and the reaction was stirred for 15 minutes until the ketone had been consumed. Water (15 mL) was added, the aqueous phase was extracted with EtOAc (2x 15 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The unpurified alcohol (231 mg, 0.687 mmol, 1.00 equiv.) was directly protected as the *p*-bromobenzoate by dissolving in pyridine (5 mL) and adding p-bromobenzoyl chloride (377 mg, 1.71 mmol, 2.5 equiv) and DMAP (83.9 mg, 0.687 mmol, 1.00 equiv.). The reaction was stirred at r.t. for 36 h, concentrated and applied directly to silica gel chromatography (gradient elution: 0-5-10-20% EtOAc/hexanes) to afford the desired product as a white solid (192 mg, 53.3% yield over three steps). Slow evaporation of a methanol solution over water at r.t. in the dark afforded single crystals suitable for X-ray analysis (see Part 3 for full details).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.87 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 5.12 (dt, J = 12.7, 4.6 Hz, 1H), 3.69 (s, 3H), 3.23 (br s, 1H), 3.08 (br q, J = 6.3 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.26 (m, 1H), 2.01 (s, 3H), 1.74 (dt, J = 12.7, 9.3 Hz, 1H), 1.29 (br d, J = 6.3 Hz, 3H), 1.18 (br s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.0, 168.5, 164.8, 149.2, 145.1, 140.8, 131.6 (2C), 131.2, 131.1 (2C), 129.4, 129.0, 128.0, 123.7, 72.3, 60.8, 31.5, 30.8, 29.0, 23.0, 20.7, 20.5, 14.7, 10.0; **IR** (thin film) 2957, 2880, 1763, 1719, 1591; **TLC R_f** 0.55 (20% EtOAc/hexanes); **$[a]_D^{25}$** +10.4 (*c*= 1.06; CH_2Cl_2); **MS** (FAB^+) calc. for $C_{25}H_{27}BrO_7Na$ (M+Na) 541, found 541; **m.p.** 135-142 °C.

b. Table 2, Entry 2 (*p*-Bromobenzoate **C**)



X-ray crystal structure analysis



The *p*-bromobenzoate derivative was prepared by the above procedure to afford the desired product as a white solid. Slow evaporation of an isopropanol solution over hexanes at r.t. in the dark afforded single crystals suitable for X-ray analysis (see Part 3 for full details).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.4 Hz, 2H), 7.65 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.45 (m, 2H), 5.27 (dt, J = 12.6, 4.6 Hz, 1H), 3.59 (br s, 1H), 3.33 (br s, 1H), 2.50 (s, 6H), 2.43 (m, 1H), 1.90 (dt, J = 12.7, 8.9 Hz, 1H), 1.47 (br d, J = 6.2 Hz, 3H0, 1.35 (br d, J = 6.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 164.8 (3C), 143.1, 141.9, 131.7 (2C), 131.1 (2C), 130.8, 129.6, 129.4, 128.1, 126.7 (2C), 126.6, 126.2, 121.5, 121.3, 72.3, 32.1, 30.7, 29.1, 23.1, 20.9, 20.7, 14.5; **IR** (thin film) 3072, 2980, 2936, 2884, 1765, 1719; **TLC R_f** 0.24 (20% EtOAc/hexanes); **[a]$_D^{25}$** -39.4 (*c*= 0.810; CH_2Cl_2); **MS** (FAB^+) calc. for $C_{27}H_{25}BrO_6Na$ (M+Na) 547, found 547; **m.p.** 208-212 °C.

Part 3. X-ray Crystallographic Data
a. Catalyst 9.

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.76 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[†††] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[‡‡‡] which corrects for Lp and decay. Absorption corrections were applied using SADABS[§§§] supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[****] program and refined by least squares method on F^2, SHELXL-97,[††††] incorporated in SHELXTL-PC V 6.10.[‡‡‡‡]

[†††] SMART V 5.625 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2001).
[‡‡‡] SAINT V 6.22 (NT) *Software for the CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2001).
[§§§] SADABS. *Program for absorption corrections using Siemens CCD based on the method of Robert Blessing*; Blessing, R.H. Acta Cryst. A51 (1995) 33-38.
[****] Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure,* University of Göttingen, Germany, 1990.
[††††] Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure,* University of Göttingen, Germany, 1997.

Data was collected on several crystals, at various temperatures and on various instruments. All data proved problematic and the best overall data set is presented here. The data is poor, but the overall structural features are satisfactory.

The structure was solved in the space group R3 (# 146) by analysis of systematic absences. Attempts to place this in a centrosymmetric space group failed and refinement of the racemic twin law resulted in a value of 0.102. Further attempts to locate different cell parameter or twin components also failed using programs such as Gemini[§§§§] and Cell_now. All non-carbon and non-hydrogen atoms are refined anisotropically. Refinement of the carbon atoms anisotropically results in many of the atoms becoming non-positive definite. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 30% ellipsoids.

[a] Obtained with graphite monochromated Mo Kα (l = 0.71073 Å) radiation. [b]$R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\{\sum[w(F_o^2)^2]\}^{1/2}$.

b. Ketone A.

CCDC-262970 contains the supplementary crystallographic data for this structure.[*****]

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.76 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[†††] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[‡‡‡] which corrects for Lp and decay. The structures are solved by the direct method using the SHELXS-97[****] program and refined by least squares method on F^2, SHELXL-97, [††††] incorporated in SHELXTL V6.10.[‡‡‡‡]

The structure was solved in the space group $P2_1$ (# 4) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsiods.

[a] Obtained with graphite monochromated Mo Kα (l = 0.71073 Å) radiation. [b]$R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c]$wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\{\sum[w(F_o^2)^2]\}^{1/2}$.

c. *p*-Bromobenzoate B

CCDC-262969 contains the supplementary crystallographic data for this structure.[*****]

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 193 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.76 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[†††] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[‡‡‡] which corrects for Lp and decay. Absorption corrections were applied using SADABS[§§§] supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[****] program and refined by least squares method on F^2, SHELXL-97, [††††] incorporated in SHELXTL-PC V 6.10.[‡‡‡‡]

[‡‡‡‡] SHELXTL 6.1 (PC-Version), *Program library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems, Madison, WI (2000).

[§§§§] Gemini (Version 1.02), *Autoindexing Program for Twin Crystals*; Bruker Analytical X-ray Systems, Madison, WI (2000).

[*****] These data can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The structure was solved in the space space group $P2_1$ (# 4). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsiods.
[a] Obtained with graphite monochromated Mo Kα (l = 0.71073 Å) radiation. [b]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\{\Sigma[w(F_o^2)^2]\}^{1/2}$.

d. *p*-Bromobenzoate C

CCDC-262971 contains the supplementary crystallographic data for this structure.[*****]

Data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 10 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.80 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[†††] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[‡‡‡] which corrects for Lp and decay. Absorption corrections were applied using SADABS[§§§] supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[*****] program and refined by least squares method on F^2, SHELXL-97, [††††] incorporated in SHELXTL-PC V 6.10.[‡‡‡‡]

The structure was solved in the space group $P2_1$ (# 4) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsoids.
[a] Obtained with graphite monochromated Mo Kα (l = 0.71073 Å) radiation. [b]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\{\Sigma[w(F_o^2)^2]\}^{1/2}$.

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